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THE MINERAL INDUSTRIES EXPERIMENT STATION

College of Mineral Industries

THE PENNSYLVANIA STATE UNIVERSITY

REPORT NO. 1

REVIEW OF FUNDAMENTAL INVESTIGATIONS OF  
SILVER OXIDE ELECTRODES

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October 1965

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University Park, Pennsylvania

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REPORT NO. 1

REVIEW OF FUNDAMENTAL INVESTIGATIONS OF  
SILVER OXIDE ELECTRODES

Submitted by

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Contract DA49-186-AMC-197(D) "Kinetic Studies of  
the Zinc-Silver Oxide-KOH Battery at Low  
Temperatures"

# 1. Review of the Silver Oxide Electrode.

## 1.1. Introduction.

Appendix 1 gives brief summaries of a number of recent papers (1 to 19) concerned with fundamental aspects of the  $\text{AgO}/\text{Ag}_2\text{O}/\text{Ag}$  electrode in alkali. Instead of reviewing these papers in turn, a description is given below of the most likely physical model of the behavior of the electrode, based on the information in these reports.

The standard-state reduction potentials of the reactions of interest are

	$E_o$ , volts
$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- = 2\text{Ag} + 2\text{OH}^-$	0.344
$\text{Ag}_2\text{CO}_3 + 2e^- = 2\text{Ag} + \text{CO}_3^{2-}$	0.47
$2\text{AgO} + \text{H}_2\text{O} + 2e^- = \text{Ag}_2\text{O} + 2\text{OH}^-$	0.60
$\text{Ag}^+ + e^- = \text{Ag}$	0.799

Higher activities of  $\text{OH}^-$  than standard state will give theoretical open circuit voltages (OCV) more negative than the values 0.344 and 0.60, by about 60 millivolts/pH at room temperature. The reactions are favored from left to right (cathodic current) by more negative potentials.  $\text{AgO}$  is a semiconductor with a high conductivity but  $\text{Ag}_2\text{O}$  has a low conductivity ( $10^{-8}$  ohm cm).  $\text{AgO}$  is insoluble in water,  $\text{Ag}_2\text{O}$  dissolves to the extent of 0.001 gm/100 ml ( $\sim 10^{-4}$  moles Ag/litre) at  $20^\circ\text{C}$ . The dissociation constant of  $(\text{Ag}^+)(\text{OH}^-) \rightleftharpoons \text{AgOH}$  is about 1/200 at  $25^\circ\text{C}$ , so that for 1 N  $\text{OH}^-$ , the  $\text{AgOH}$  is only slightly dissociated. It seems probable that the concentration of free  $\text{Ag}^+$  in electrolyte near the  $\text{Ag}_2\text{O}-\text{Ag}/\text{KOH}$  electrode at open circuit is about  $10^{-6}$  molar.

## 1.2 Models of Behavior During Charge and Discharge.

It is possible that the anodic charging of solid silver could produce a situation (Model 1) as illustrated in Figure 1. On passing anodic current the potential would rise rapidly to the  $\text{Ag}_2\text{O}$ -Ag potential (first potential plateau) and a thin, compact film of  $\text{Ag}_2\text{O}$  would be formed on the Ag. Because of the low conductivity of  $\text{Ag}_2\text{O}$  the electrode would be rapidly passivated (this is an example of "chemical passivation" by a very thin film) and the potential would increase until the reaction  $\text{Ag}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{AgO} + 2\text{OH}^-$  occurred (second plateau), giving a conductive film. Further oxidation would produce movement of the Ag/AgO boundary into the solid, with no more than a thin film of  $\text{Ag}_2\text{O}$  separating Ag and AgO. Since large amounts of  $\text{Ag}_2\text{O}$  are often present in practice, it has been postulated that the non-electrochemical reaction  $\text{AgO} + \text{Ag} \rightarrow \text{Ag}_2\text{O}$  can occur. Since the layers are relatively impermeable to electrolyte, continued conversion of Ag to AgO occurs by transfer of  $\text{Ag}^+$  or  $\text{O}^{2-}$  through the solid. For thick layers, this rate eventually becomes insufficient to maintain the current and the potential gradually changes to oxygen evolution (gassing). Alternatively charge at a fixed potential would be controlled by electrochemical kinetics and/or mass transfer when the oxide layers were thin, but as IR and mass transfer resistance in the layers increase, the current would fall off to low values.

On discharge at potentials between 0.6 and 0.35 (first discharge plateau), AgO would form  $\text{Ag}_2\text{O}$ , which again leads to passivation until the electrode potential falls to a point where  $\text{Ag}_2\text{O} \rightarrow \text{Ag}$  (second discharge plateau), giving suitable conductivity by a bridge of Ag between electrolyte and AgO.

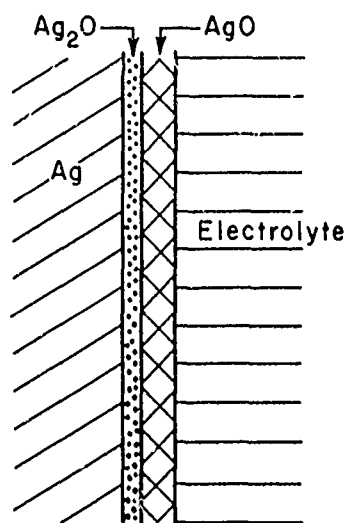


Fig. 1

Illustration of Model I, for Charge of a Silver Electrode.

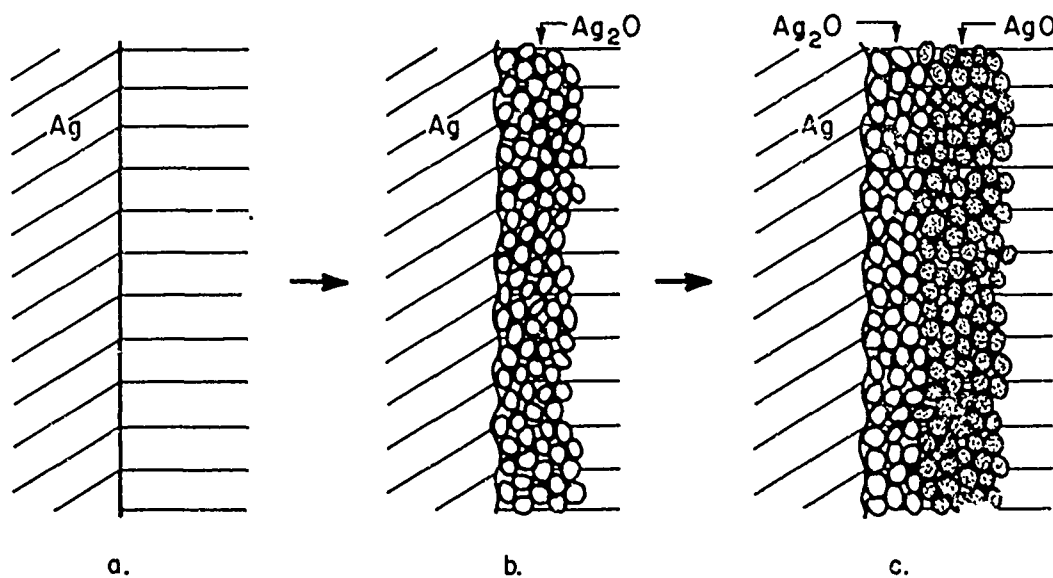


Fig. 2

Illustration of Model 2, for Charge of a Silver Electrode.

Since the density of Ag is higher than that of the oxides (Ag, 10,  $\text{Ag}_2\text{O}$ , 7.14,  $\text{AgO}$ , 7.44), the discharged surface might be somewhat spongy. On recharge, the interior of the sponge would be utilized and repeated cycling would produce an active, high area, electrode.

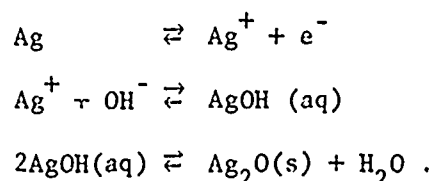
Although this model is feasible, there is considerable experimental evidence that it is not a true picture. The work of Wales and Burbank (43) indicates that massive rearrangement of Ag,  $\text{Ag}_2\text{O}$ , and  $\text{AgO}$  occurs on charge and discharge, with formation of discrete crystals of the components. The model from their work (Model 2) is illustrated in Figure 2. On charge, the solid silver is transferred and transformed to crystals of  $\text{Ag}_2\text{O}$  in the first charge plateau. When this has built up to a certain thickness (about 1.5 microns in the work quoted),  $\text{Ag}_2\text{O}$  is transferred and transformed into crystals of  $\text{AgO}$  (second charge plateau) in a region at the surface next to the bulk electrolyte. (This is an example of "mechanical passivation, where a thick, porous layer is produced before passivation occurs.) Since the layers of crystals are permeable to electrolyte, the solid silver can still react to form more  $\text{Ag}_2\text{O}$ , so that the charge added in the second plateau is considerably more than that corresponding to  $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ . Eventually, the charge cannot be maintained at constant current by a reasonable potential and oxygen evolution potentials are reached. (This occurred at a crystal layer thickness of about 8 microns. A slow charge (low rate of charge) produced larger crystals but gave bigger conversion of Ag to  $\text{AgO}$  before gassing.)

On discharge at the first plateau,  $\text{Ag}_2\text{O}$  is formed as separate crystals from  $\text{AgO}$  at the surface. Since the crystal layers are permeable to electrolyte, the region in which this occurs is considerably thicker



than a mono-molecular layer and the first plateau represents about 20% of the available charge. Eventually the potential falls to the point where  $\text{Ag}_2\text{O}$  can discharge and this potential is held while  $\text{AgO}$  and  $\text{Ag}_2\text{O}$  are discharging. Towards the end of the discharge only  $\text{Ag}_2\text{O}$  is present. (Large discharge currents produced small crystals of  $\text{Ag}$ , in a layer which was open and permeable. This layer had good charge acceptance on recharge.)

Several questions can be asked about model 2. Firstly, what causes the massive transfer of components from one crystal to another at the high rates observed? It would appear necessary to postulate transfer via a dissolved intermediate, for example



Secondly, what causes the reduction in rate-of-charging as the thickness of the surface layers increase? (Either increase of potential at constant  $i$ , or decrease in  $i$  at constant  $V$ .) If the surface layers are porous and permeable, the electrolyte reaches underlying silver and there seems no reason why charge should not be carried out to complete conversion. The situation is illustrated in Figure 3, for the charge of a porous layer of  $\text{Ag}$  crystals on solid  $\text{Ag}$ . When charging current is switched on the silver does not charge to any significant extent until the  $\text{Ag}/\text{Ag}_2\text{O}$  potential is reached. Then the surface of the layer is charged and since the ions have only a short distance to travel, the IR polarization is low, as shown in curve a. As the external crystals become converted to  $\text{Ag}_2\text{O}$ , the ions have to travel further to reach unreacted silver crystals and IR polarization increases, b, until either the  $\text{Ag}_2\text{O}/\text{AgO}$  potential is reached, or there

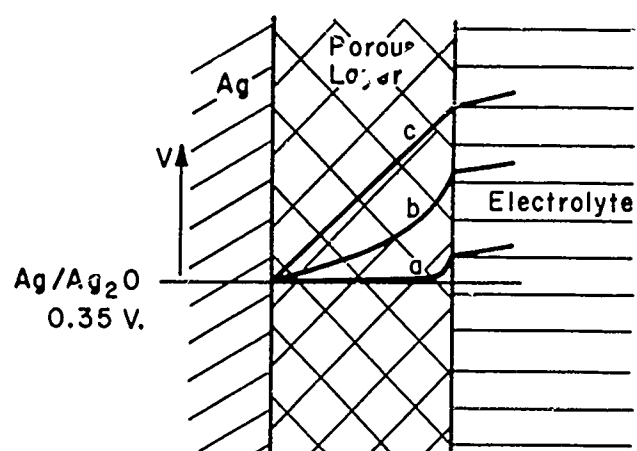
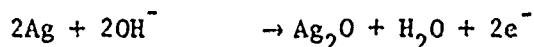
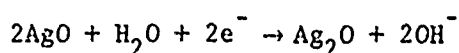


Fig. 3

Illustration of Build-Up of Potential due to IR Polarization in a Porous Layer.

is only the solid silver left unreacted, c. In this last case, the low area may lead to activation polarization and the voltage will go to the  $\text{Ag}_2\text{O}/\text{Ag}$  potential. As soon as this potential is reached, some of the current is supported by  $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ , which does not initially require higher IR polarization. The second charge plateau is then obtained, which in time goes through a similar process to reach the gassing potential. (Mass transfer limitations of  $\text{OH}^-$  through the layer will give rise to similar effects.) Theoretically, a low charging current should enable the first plateau to extend over almost 50% of the total charge and should enable the crystal layer to be converted completely to AgO before gassing. A high charging current gives a steep potential gradient through the porous layer, and Ag,  $\text{Ag}_2\text{O}$ , AgO will exist until the porous layer is charged completely to AgO.

If charge is stopped before the porous layer is charged completely to AgO, the exterior of the porous layer tends to come the equilibrium potential of  $\text{AgO}/\text{Ag}_2\text{O}$ , while the interior tries to reach the  $\text{Ag}_2\text{O}/\text{Ag}$  potential. The electrode cannot be at both potentials at once and the reactions



proceed at zero net current until (a) nearly all of the Ag has gone and the potential is that of  $\text{AgO}/\text{Ag}_2\text{O}$ , or (b) nearly all of the AgO has gone and the potential is that of  $\text{Ag}_2\text{O}/\text{Ag}$ , depending on the relative proportions of Ag,  $\text{Ag}_2\text{O}$ , AgO when the charge is cut off.

One of the major differences between model 1 and model 2 is that in model 1 the formation of  $\text{Ag}_2\text{O}$  forms an electronically insulating

film between Ag and the electrolyte, so that reaction cannot proceed until the potential rises to values at which  $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ . In model 2,  $\text{Ag}_2\text{O}$  is formed as distinct crystals which allow electrolyte to penetrate to unreacted silver, so that a layer of  $\text{Ag}_2\text{O}$  does not form an electronically insulating shield between Ag and electrolyte. It seems probable to us that the true situation is a combination of these models. A "combination model" might operate as follows. On charging, the silver surface (either of plane solid or of preformed crystals) forms  $\text{Ag}_2\text{O}$  as a surface film. However, this film is not stable and it breaks down due to solubility and dynamic electrochemical reactions to form separate crystals of  $\text{Ag}_2\text{O}$ . The break-down leaves underlying Ag exposed for further reaction and for electronic conduction. Fast rates of charging on large crystals tends to produce more rapid production of surface film than break-down, leading to a rise to the  $\text{Ag}_2\text{O}/\text{AgO}$  potential at low fractional conversions of Ag to  $\text{Ag}_2\text{O}$ . A low porosity and permeability of the crystal layer accelerates the rise by the model 2 effect. Slower rates of charge increase the fraction of charge in the first plateau, but lead to large crystals of  $\text{Ag}_2\text{O}$  and, eventually, AgO. On discharge, the reverse effect occurs; at high rates of discharge, an  $\text{Ag}_2\text{O}$  film is formed on the crystals and the potential drops rapidly to the  $\text{Ag}_2\text{O}/\text{Ag}$  potential. The new crystals formed during discharge are smaller at high discharge rates.

Two opposing effects are present. At low rates of charge, the crystals produced are large and the layer is permeable, giving bigger conversion of solid Ag to oxides. The bigger crystals, however, give a less active surface on discharge. High rates of charge produce smaller crystals which form a less permeable surface layer, thus blocking off

underlying Ag. On discharge, the small crystals give high electrochemical rates and rates of surface dissolution ( $\text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O} \rightarrow 2\text{AgOH}(\text{aq}) \xrightarrow{2\text{e}^-} 2\text{Ag}(\text{s}) + 2\text{OH}^-$ ), but IR or mass transfer loss through the impermeable layer is high. It is predicted, therefore, that there exists an optimum charging rate and pore size of the electrode.

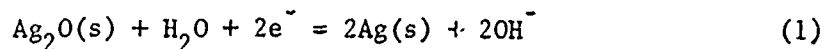
Practical battery electrodes are not, of course, made by charge-discharge production of porous layers on a solid silver surface. Ag or AgO powder is packed into a supporting metal grid to give a preformed porous electrode, with the grid acting as the current collector. The massive transfers of Ag during cycling explain the loss of structural strength of porous electrodes, the loss of adherence to the supporting screen, the presence of silver in the electrolyte [ $\text{Ag}_2\text{O}(\text{aq}) \rightarrow 2\text{Ag} + \frac{1}{2}\text{O}_2$ ] and the variation of performance with depth of discharge, rate of discharge and number of cycles.

### 1.3. Surface Electrochemistry of the $\text{Ag}_2\text{O}/\text{Ag}$ Electrode.

The above general description of the processes occurring at silver oxide electrodes is an interpretation and combination of results and explanations given in the literature. There is little work in the literature on the basic electrochemical parameters of the electrodes. This is not surprising, because the above discussion shows that the surface of an electrode is constantly changing and, consequently many of the normal electrochemical tests are not directly applicable. The possible mechanisms of the surface reactions are, therefore, discussed here as a guide to experimental design rather than as an explanation of existing experimental results.

Considering the reaction of primary interest in our work, the

over-all process is



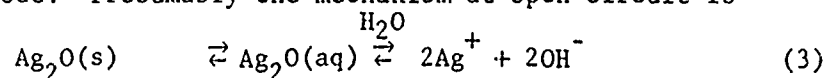
In this form, it would be expected that the rates and, hence, the open circuit potential would depend on the relative surface areas (activities) of  $\text{Ag}_2\text{O}$  and Ag. For example, it is known that anodic oxidation of platinum,



starts to occur on bare platinum at about 0.7 volts (versus standard hydrogen in the same electrolyte). The initial discharge produces a layer of chemisorbed oxygen which passivates the electrode to some extent. On prolonged anodic oxidation, surface oxygen is gradually incorporated into the metal lattice to form an oxide film up to about 10 monolayers thick. The thickness of this layer depends on the anodisation potential, but the film can be formed at potentials below that of oxygen evolution. When the oxidized surface is left at open circuit, it does not rapidly return to a fixed potential but gradually drifts to lower potentials (to about 0.8 to 0.9 volts). It has been concluded that the standard state free energy of reaction 2 is variable depending on the thickness of the film, and that the amount of covered and uncovered metal area also affect the electrode potential at open circuit.

On the other hand, when Ag is first anodised, the electrode reaches a definite potential and stays at this potential at open circuit. A layer of chemisorbed oxygen may be formed on discharge but it is rapidly incorporated into the lattice; further anodisation produces  $\text{Ag}_2\text{O}$ . Providing the electrode contains Ag and  $\text{Ag}_2\text{O}$ , the open circuit potential is near 0.344, irrespective of the relative amounts of these materials. The electrode behaves as an "electrode of the second kind" and can be used as a standard

reference electrode. Presumably the mechanism at open circuit is



Under fixed conditions, the activity of  $\text{Ag}^+$  is fixed by the solubility and dissociation constant of silver oxide, and the electrode potential is determined by the equilibrium of reaction 4. If forward and backward rate equations are written for reactions 3 and 4, the surface activity (area) of  $\text{Ag}_2\text{O}(\text{s})$  occurs in both reactions of 4, and  $\text{Ag}(\text{s})$  in both reactions of 3, so that at open circuit (zero net rate) the surface activities cancel. No dependence of potential on surface areas is present, providing significant quantities of crystalline  $\text{Ag}_2\text{O}$  and  $\text{Ag}$  are present.

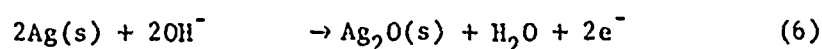
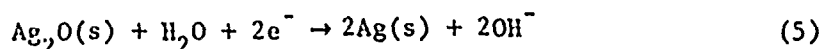
The reactions are in dynamic equilibrium at open circuit and it is likely that the surface of an  $\text{Ag}/\text{Ag}_2\text{O}$  electrode changes with time even at zero net current. It is to be expected that small crystallites and more randomly oriented atoms will dissolve and reprecipitate, leading to a slow growth of larger and more ordered crystals. It does not appear to have been established whether dissolved  $\text{Ag}_2\text{O}$  will crystallize readily on  $\text{Ag}$ , but conventional theories of nucleation predict that if  $\text{Ag}_2\text{O}$  starts to form on a silver nucleation site, it will continue to grow as a discrete  $\text{Ag}_2\text{O}$  crystal bonded to the silver at the original site. Thus,  $\text{Ag}_2\text{O}$  is expected to prefer to recrystallize on existing  $\text{Ag}_2\text{O}$  rather than cover the entire electrode surface with  $\text{Ag}_2\text{O}$  bonded to silver atoms.

An essential feature of a reference electrode of this kind is that it only maintains the reference potential when the electrode current is too small to (a) give activation polarization of reaction 4,  $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$  or (b) give concentration polarization of reaction 3. In the latter

instance, cathodic current removes  $\text{Ag}^+$  and  $\text{Ag}_2\text{O}$  has to dissolve fast enough to maintain a saturated solution. Anodic current produces  $\text{Ag}^+$  and this must react and deposit as  $\text{Ag}_2\text{O}$  fast enough to prevent super-saturation of the electrolyte. Hydroxyl ion also has to be transported at sufficiently rapid rates to balance the reactions.

When the electrode is used at high current densities, activation and concentration polarization will arise and the degree of polarization depends on the areas of  $\text{Ag}_2\text{O}$  and  $\text{Ag}$  in contact with electrolyte. If the dissolution-crystallization reaction, reaction 3, were fast and the  $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$  reaction activated, the rate at a given polarization would be dependent on the area of  $\text{Ag}$ . Cathodic current produces more  $\text{Ag}$  and the area of  $\text{Ag}$  would increase with discharge, leading to an autocatalytic effect. If current were high enough to produce build-up of  $\text{OH}^-$  at the electrode, the concentration of  $\text{Ag}^+$  would decrease according to the equilibrium  $\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{Ag}^+ + 2\text{OH}^-$ , and polarization would increase. In electrolytes of high pH (30 weight %  $\text{KOH}$  for example), this effect should not increase polarization by more than about 100 mV even under extreme conditions. If reaction 4 were fast and 3 slow, cathodic current would lead to depletion of  $\text{Ag}^+$  and, eventually, a limiting current corresponding to the irreversible dissolution of  $\text{Ag}_2\text{O}$ . Polarization would be less for higher areas of  $\text{Ag}_2\text{O}$ , and increased discharge would increase polarization.

There is no guarantee that the reactions which determine the open circuit potential are necessarily those which occur at high current density. There seems no reason why rapid charge or discharge should not lead to direct reactions such as those occurring at platinum,





Both of these reactions may involve activation polarization, with reaction 5 aided by high  $\text{Ag}_2\text{O}$  area and reaction 6 aided by high Ag area. For example, if the dissolution of  $\text{Ag}_2\text{O}$  is relatively slow, a high current density will rapidly discharge dissolved  $\text{Ag}_2\text{O}$  and  $\text{Ag}^+$ . Even if the electrolyte is saturated with  $\text{Ag}_2\text{O}$ , the steady limiting current will be

$$i_L = 2FrA + kC \quad (7)$$

where  $i_L$  is the limiting current density per unit plane area of electrode;  $r$  is the maximum rate of dissolution of  $\text{Ag}_2\text{O}$  per unit true area;  $A$  is the true area of  $\text{Ag}_2\text{O}$  per unit plane area;  $k$  is a mass transfer factor for  $\text{Ag}_2\text{O}$  through electrolyte to the electrode, per unit plane area;  $C$  is the concentration of dissolved  $\text{Ag}_2\text{O}$  in the bulk of the electrolyte.  $k$  is probably about  $60 \text{ mamp/cm}^2$  per gm mole  $\text{Ag}_2\text{O}$  per litre, for unstirred electrolytes. Since  $C$  is about  $10^{-4}$  molar,  $kC$  is less than  $1 \text{ mamp/cm}^2$  plane area. Therefore, if  $r$  is low, the electrode will polarize at high current density until reaction 5 occurs. On shutting off the current, the open circuit potential is less than theoretical because of the depletion of  $\text{Ag}^+$ ; it may be determined at first by the relative rates of reactions 5 and 6, but will drift to ideal values as  $\text{Ag}_2\text{O}$  dissolves and establishes a saturated solution of  $\text{Ag}^+$ .

The primary difference between reactions 3, 4 and reactions 5, 6 is that in the former, reduction (production of Ag) occurs via a dissolved intermediate while in the latter it is produced directly. The theoretical OCV of the former is fixed, while in the latter it will vary depending on the relative amounts of  $\text{Ag}_2\text{O}$  and Ag which are present.

## 2. Experimental Program

### 2.1. Design of Experiments.

Based on the previous discussion of the possible modes of

operation of the  $\text{Ag}_2\text{O}/\text{Ag}$  electrode, the following experimental methods are suggested. To simplify the system it is desirable to eliminate effects of porosity. Whenever a porous electrode is used, the problem of distributed effects arise; at high current densities reaction is concentrated in the outer layers, and transient methods are particularly difficult to apply. On the other hand, charging of a solid silver electrode probably produces, at first, a surface layer of chemisorbed oxygen. A steady theoretical OCV can only be obtained when there is a sufficient quantity of  $\text{Ag}_2\text{O}$  present to saturate electrolyte near the electrode and give a free energy corresponding to bulk  $\text{Ag}_2\text{O}$ . To form sufficient  $\text{Ag}_2\text{O}$  on a solid electrode requires cycling, with the inevitable production of porous layers. To overcome these problems, an electrode was pressed from a mixture of  $\text{Ag}_2\text{O}$  and Ag powder and impregnated with epoxy resin to fill in the pore structure. This electrode gave good conductivity and did not gain weight on immersion in electrolyte.

To avoid massive rearrangement of the surface structure during testing, transient galvanostatic tests were made to establish polarization at low states of discharge of the surface. The results from these tests are given in Section 2.3. The results of pseudo steady-state tests, with potential measured two minutes after changing the current are also reported. Triangular voltage sweep methods have also been employed, but insufficient results have been obtained to be worth reporting.

Experiments to be performed include the measurement of the rate of dissolution of  $\text{Ag}_2\text{O}$  at a rotating electrode. It may be possible to obtain the mass transfer factor  $k$  of equation 7 as a function of speed of rotation, and the limiting rate of dissolution,  $r$ , at high rotation

speeds. In addition, transient galvanostatic tests at high current densities will be used to obtain transition times. (At the moment, the current densities obtained from the test electrode are limited by the maximum current capability of the Wenking potentiostat. Smaller electrodes are being prepared to give higher current densities.) The rate of change of potential on current interruption will be investigated, with a primary aim of determining whether high ohmic resistance develops during discharge of the electrode.

## 2.2. Experimental

### 2.2.1. Preparation of Electrodes

#### Ag/Ag<sub>2</sub>O Test Electrode

Solid, non-porous, Ag/Ag<sub>2</sub>O electrodes were prepared by pressing a mixture of Ag and Ag<sub>2</sub>O powder (average particle size 5-10 $\mu$ ) (Fisher) and impregnating the resultant pellet with an epoxy resin. The exact procedure was as follows: Approximately  $\frac{1}{2}$  gram each of Ag and Ag<sub>2</sub>O were weighed into an amber bottle which was then shaken on a Spex #8000 shaker for fifteen minutes. The mix was transferred to a die (standard KBr pellet type) and evacuated for two minutes prior to pressing at 90,000 lbs/in<sup>2</sup> for two minutes. This gave a pellet 1.300 cm in diameter (area = 1.327 cm<sup>2</sup>) with a porosity of about 15 percent (based upon the calculated and measured densities of the pellet). The porosity as determined from water absorption in vacuum was about 10 percent indicating a closed pore volume of about five percent. The pellet was impregnated under vacuum with a low viscosity, room-temperature cure, epoxy resin (Eccoseal W19 and Catalyst 11, Emerson and Cuming, Canton, Mass.) to render it non-porous. There was no change in weight of the pellet

following its exposure to water (in vacuum) for about two hours, which indicated that it was non-porous. The  $\text{Ag}/\text{Ag}_2\text{O}$  pellet was then mounted (with the previously used epoxy resin) in a  $5/8$ " long lucite cylinder with one face of the approximately 1 mm thick pellet flush with one end of the lucite cylinder. The other face of the pellet, with a Pt wire pressed against it, was coated with epoxy resin. Once the resin had cured, a four inch long Teflon cylinder was slipped over the Pt wire and press-fitted into the lucite cylinder. Prior to placing the electrode into the electrochemical system the  $\text{Ag}/\text{Ag}_2\text{O}$  face was cleaned with a water slurry of #600 silicon carbide grain (Carborundum Co., Niagara Falls, N. Y.).

Although tests (visual observation and weight measurements) indicated that the resin was unaffected by exposure to the aqueous KOH electrolyte of the system, it would have been desirable to avoid the use of the resin thereby avoiding the possibility of introducing impurities into the system. For this reason a considerable amount of time was initially expended in trying other methods of preparing non-porous electrodes. These methods included grinding of the Ag and  $\text{Ag}_2\text{O}$  to obtain smaller particle sizes and adding finely powdered Teflon and polyethylene to the mixes. In some cases electrodes with close to zero percent porosity were obtained. However, these electrodes had very high electrical resistances.

#### Counter Electrode

A long length of Ag wire in the form of a spiral was used as the counter electrode. This spiral was contained in a lucite cylinder with a piece of microporous plastic (Millipore #OSWP037PO, Bedford, Mass.) sealed into the solution end by a Teflon washer. The purpose of the

plastic was to minimize any diffusion of oxygen from the counter electrode to the test electrode. Under most conditions, however, only  $\text{Ag}_2\text{O}$  and  $\text{AgO}$  and not oxygen were formed at the counter electrode. In addition, at intervals the spiral was cleaned of silver oxides to obtain a fresh silver surface.

#### Reference Electrode

A  $\text{Hg}/\text{HgO}/\text{KOH}(\text{aq.})$  electrode was used as the reference electrode. The aqueous  $\text{KOH}$  was of the same concentration as that used in the test cell, to eliminate liquid junction potentials.

#### 2.2.2. Apparatus, Reagents, and Procedures.

Galvanostatic control, in both the steady state and unsteady state measurements, was maintained with a Wenking potentiostat (Fast Rise Model #61/R). In the steady state measurements, a modified Beckmann Model 9600 pH meter (full scale voltage ranges of 0.07, 0.14, 0.28, 0.70, and 1.4 volts) was used to measure the voltages between the test and reference electrodes as a function of current. The current was calculated from the known voltage applied to the control circuit of the potentiostat. (A precision resistor in the control circuit was also in series with the half-cell under test. The voltage developed across this resistor ( $V$ ) was equal to  $IR$  where  $I$  = current through half-cell,  $R$  = resistance of precision resistor and  $V = -(\text{applied voltage})$ , since the net potential in the control circuit must equal zero.) In the unsteady state measurements, a Tektronix Type 561 Oscilloscope (Type 63 amplifier and Type 2B67 time base) and a Polaroid camera were used to record the voltage-time traces. The potentiostat was programmed to generate a square wave current pulse (rise time  $< 2\mu\text{sec}$ ) by coupling it

with a Hg-wetted relay and a Type 250 Exact Function Generator (Exact Electronics, Hillsboro, Oregon). The relay and function generator, in combination with a voltage source, delivered a square wave potential pulse (lasting anywhere from ~3msec to 15 min) to the control portion of the potentiostat, which in turn generated a constant current pulse.

A Keithley voltmeter (Model 660) with a 0.02% limit of error was used to calibrate the voltage-measuring instruments and the various voltage sources that were used. In the unsteady state measurements, a bucking voltage (derived from a Hg cell) was applied between the reference and test electrodes so that the net potential between these electrodes was zero at open circuit. This made it possible to use the more sensitive ranges of the oscilloscope to measure small values of polarization.

A 250 ml beaker with a lucite cover was used as the electrochemical cell. The lucite cover contained five holes, three for the test, counter and reference electrodes, one for a  $N_2$  inlet tube to exclude  $O_2$  from the cell, and one for a glass tube containing a Chromel P-Alumel thermocouple for measuring the temperature of the electrolyte. The electrolyte was a 31 wt % (7.2M) aqueous solution of KOH. It was prepared by diluting 308 ml of 45 wt % KOH (Fisher Reagent) to 500 ml.

A Tenney Jr. Test Chamber (Model TJR,  $-100^{\circ}F$  to  $350^{\circ}F$  temperature range) was used to control the temperature of the cell to within  $\pm 0.25^{\circ}C$ . The one-turn temperature control potentiometer ( $200 \Omega$ ) provided with the instrument was replaced by a 10-turn Beckmann Helipot, which greatly facilitated setting the temperature of the test chamber to the desired value. Electrical contact to the electrodes was made via electrical through-put terminals on the wall of the chamber. Nitrogen

to the cell was supplied via a port in the wall, which also contained an exit line for the  $N_2$ .

The  $N_2$  was first bubbled through a 31% KOH solution outside of the chamber. In the test chamber it was passed through a long coil of Cu tubing to bring it to the temperature of the chamber, and then through another bubbler containing 31% KOH before it entered the cell.

For both steady-state and unsteady-state measurements, the cell was assembled with the test electrode raised above the level of the electrolyte, which was deaerated (usually overnight). The test electrode was then lowered into the electrolyte.

In the steady-state measurements, values of voltage were determined after two minutes at a particular current. These measurements were performed at 25°C. In the unsteady state measurements galvanostatic pulses of approximately  $\frac{1}{2}$  second duration and ranging in value from 10 ma to 200 ma were applied to the test electrode at temperatures of 24°C, 10°C, -5°C, and -20°C.

## 2.3. Results

### 2.3.1. Steady-State Measurements

When a constant cathodic current was applied to the test electrode it was found that at relatively low currents ( $i \leq 1 \text{ ma/cm}^2$  and  $i/i_L \leq 0.005$ ) a steady state condition was rapidly attained. At higher currents this was not the case. Instead, there was a slow but steady increase in polarization with time and it did not appear that a steady state condition could be attained. After some time at these higher currents it was found that the surface of the electrode had lost its original satiny lustre and had accumulated a black film, which was

readily removed by light abrasion. It seems reasonable to suppose that this black film was freshly formed silver. The inability to attain a steady state was undoubtedly related to the change in the surface of the electrode. In order to attach some significance to the time-dependent values of  $\eta$  it was decided to measure  $\eta$  at two minutes after the application of a particular constant current. This led to a series of pseudo-steady-state polarization curves which are shown in Figure 4. A considerable amount of hysteresis is evident in these measurements, and it appears that under the conditions of the measurements there is an irreversible change in the system. It should be noted that neither the limiting current region nor the values of  $V$  at any particular current were affected by the rate of stirring of the electrolyte. This indicates that rate limitations due to solution mass transport effects were not significant in this system.

Figure 5 is a plot of voltage vs time following a complete scan (open circuit to  $i_L$  and back to open circuit). Even after  $2\frac{1}{2}$  hours at open circuit, the voltage has not returned to the reversible potential ( $E_r$  at  $25^\circ\text{C}$  for  $\text{Ag}/\text{Ag}_2\text{O}/\text{KOH}(\text{aq.})/\text{HgO}/\text{Hg} = 0.244$  volts).

#### 2.3.2. Unsteady-State Measurements

The unsteady-state measurements, in contrast to the pseudo-steady-state measurements, were reproducible and exhibited no hysteresis. For example, in one day measurements were performed at temperatures of  $24^\circ\text{C}$ ,  $10^\circ\text{C}$ ,  $-5^\circ\text{C}$ , and  $-20^\circ\text{C}$ . The next day measurements at  $24^\circ\text{C}$  were in excellent agreement with those of the previous day. In addition, at any time in the course of the measurements a particular measurement could be duplicated.



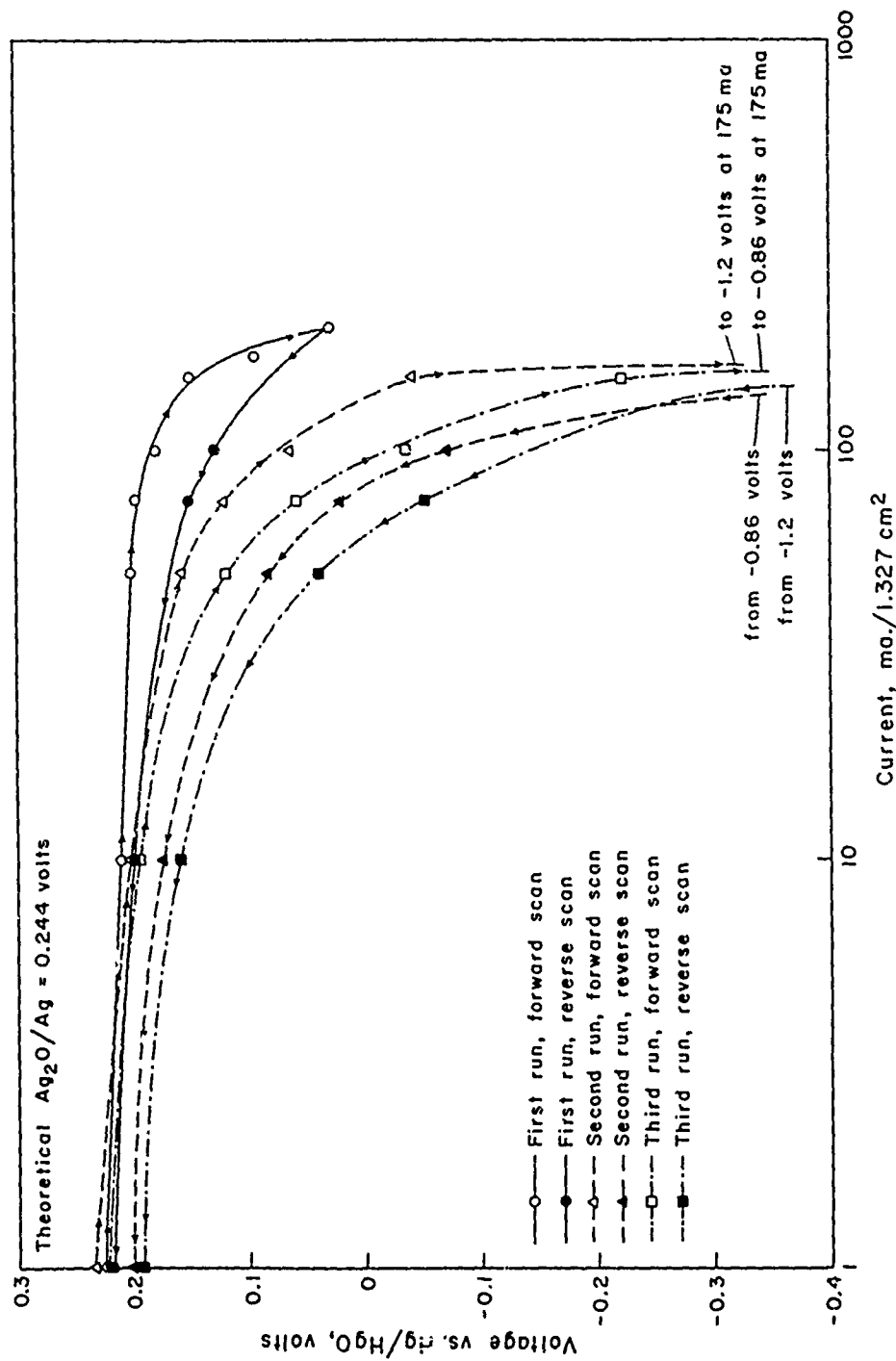


Fig. 4

Pseudo-Steady-State Current-Voltage Curves for  
the Cathodic Reduction of the  $\text{Ag}/\text{Ag}_2\text{O}/\text{KOH}$  (31% ag.) Half-Cell

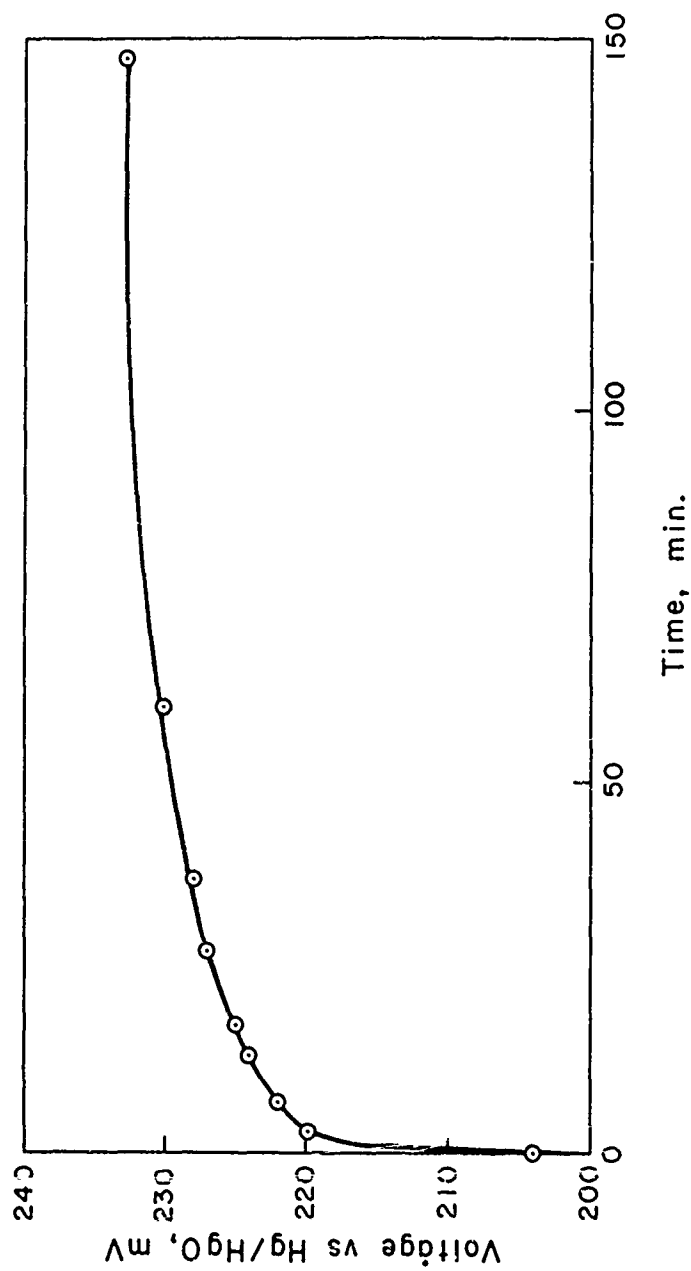


Fig. 5

Voltage of the Ag/Ag<sub>2</sub>O/KOH (31% aq.) Half-Cell at Open Circuit as a Function of Time Following a Pseudo-Steady-State Current-Voltage Curve.

A typical oscilloscopic voltage-time trace is shown in Figure 6. Extrapolation of the linear portion of the curve to time = 0 and correction for  $\eta_{IR}$  gives the polarization due to electrochemical reaction alone ( $\eta_{act.}$ ). The results of these measurements are given in Table 1 and Figure 7.

Table 1  
Results of Unsteady State Galvanostatic Measurements

Temp. °C.	i, ma.	Polarization		Resistance, $\Omega$
		$\eta_{IR}$ , mV.	$\eta_{act.}$ , mV.	
24	20	10.2	7.6	0.56
	50	26.0	16.9	0.52
	100	54.0	31.1	0.54
	200	111	42.7	0.56
10	20	10.4	10.7	0.52
	50	28.0	22.9	0.56
	100	61.1	34.9	0.61
	200	117	40.0	0.59
-5	20	13.3	14.0	0.67
	50	32.0	30.9	0.64
	100	64.0	46.0	0.64
-20	20	14.7	24.0	0.74
	50	40.0	48.2	0.80
	100	76.0	-	0.76

Assuming that the electrochemical reaction is a simple one-electron transfer reaction it is possible to calculate the exchange current ( $i_0$ ) as a function of temperature from the equation  $i = i_0 F \eta / RT$ , for small values of  $\eta$ . The results of these calculations (see Table 2) must be considered to be in some doubt since not many points were obtained for small values of  $\eta$ .

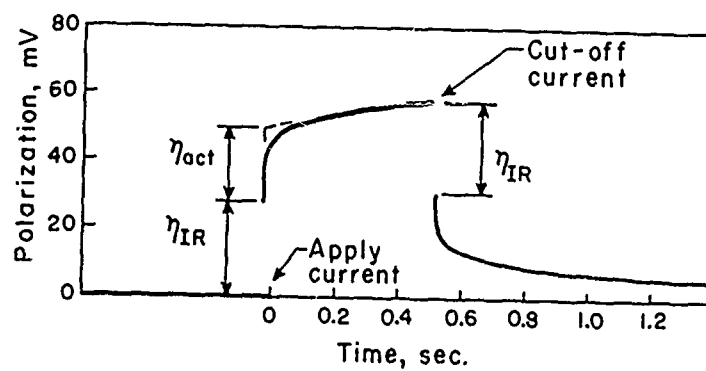


Fig. 6

Typical Galvanostatic Voltage-Time Curve for the Cathodic Reduction of the  $\text{Ag}/\text{Ag}_2\text{O}/\text{KOH}$  (31% aq.) Half-Cell.

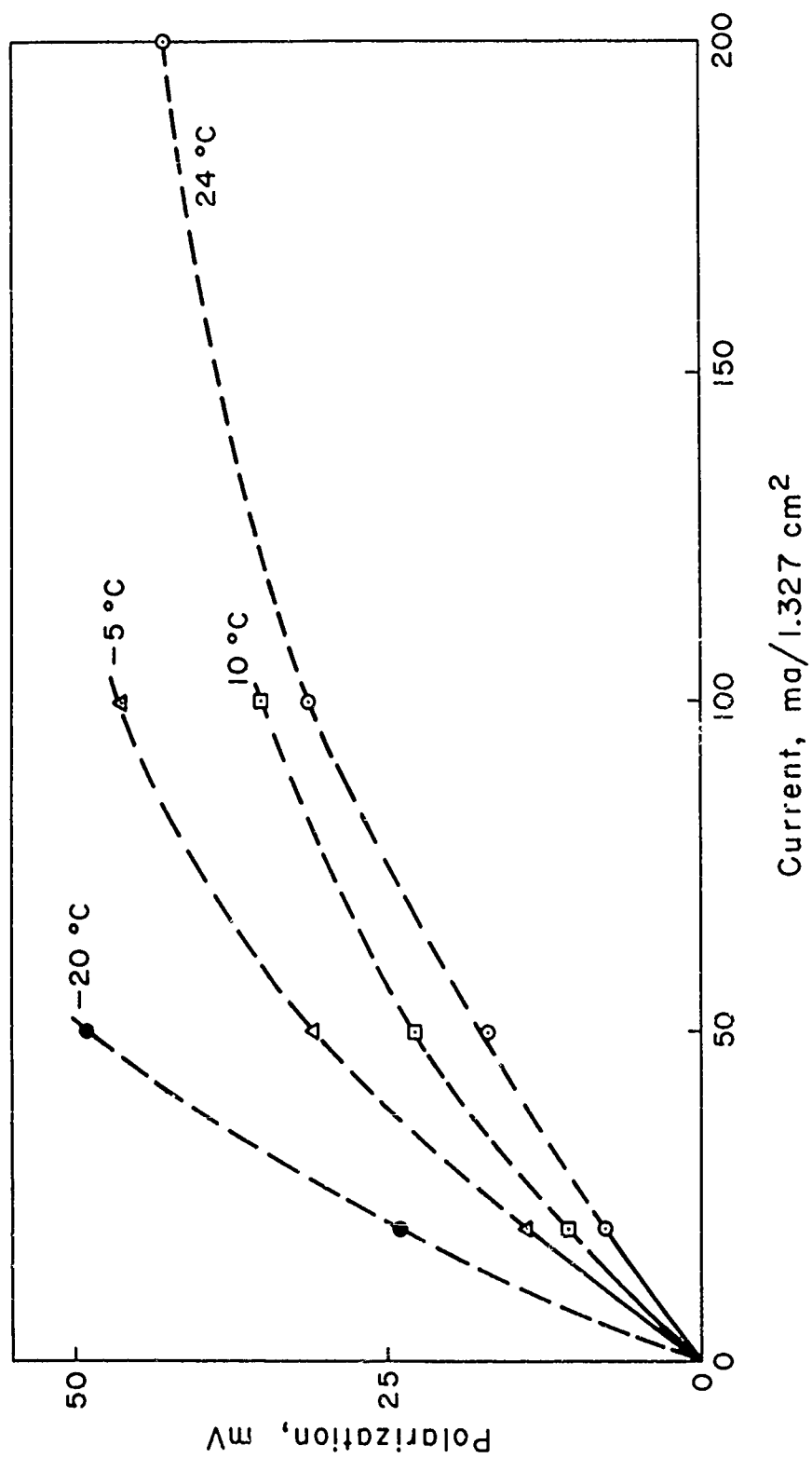


Fig. 7

Current-Voltage Curves from Unsteady-State Galvanostatic Measurements at 24°C, 10°C, -5°C, and -20°C.

Table 2

Exchange Currents for the Cathodic Reduction of the  $\text{Ag}/\text{Ag}_2\text{O}/\text{KOH}$   
(31% aq.) Half-Cell as a Function of Temperature

Temp. °C	$i_o$ ma/cm <sup>2</sup>
24	50.9
10	34.3
- 5	23.5
-20	13.7

A plot of  $\log i_o$  vs  $1/T$  gave a good straight line (see Figure 8), so if it is assumed that the same mechanism applies in the Tafel region it is possible to calculate the activation energy for this electrochemical step according to the equation,

$$\log i_o = -\left[\frac{\Delta H_o^* - \alpha F E_r}{2.3R}\right] + \text{constant}$$

This gives a value of 8.2 kcal/mole (assuming  $\alpha = \frac{1}{2}$ ), which is the chemical activation energy for zero potential across the double layer, assuming the variation of  $E_r$  with temperature to be negligible. The over-all activation energy,  $\Delta H_o^* - \alpha F E_r$ , is 4.1 kcal/mole.

#### 2.4. Discussion of Results and Conclusions.

The first conclusion which can be drawn from the results is that the  $\text{Ag}_2\text{O}/\text{Ag-KOH}$  electrode can pass relatively large currents with less than 0.1 volts activation polarization (see Figure 7). Any activation polarization present must show up in Figure 7, although it is possible that the apparent exchange current might depend on other factors than pure activation effects. The apparent exchange currents measured in the work may be lower than true exchange currents, but cannot be higher. A porous

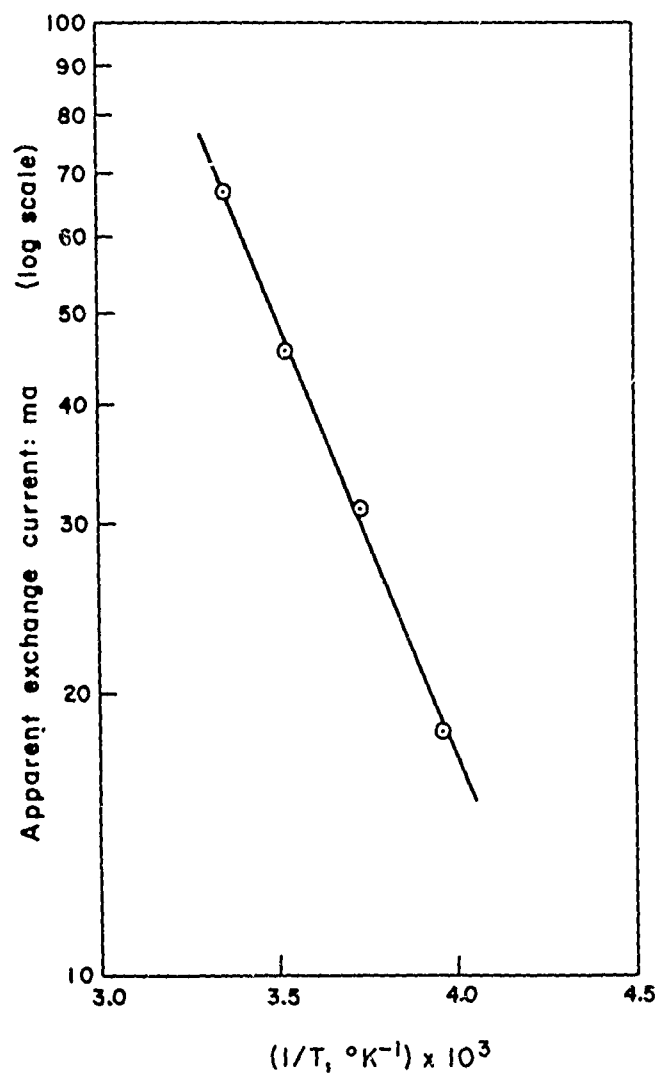


Fig. 8

Exchange Current of the Ag/Ag<sub>2</sub>O/KOH (31% aq.)  
Half-Cell as a Function of Temperature.

electrode with a high internal area per unit apparent area (A.A.) should be capable of delivering large initial currents with relatively little activation polarization. The exchange current density obtained by extrapolation of Figure 8 to  $-54^{\circ}\text{C}$  is  $5.1 \text{ ma/cm}^2$ . At a current density of  $380 \text{ ma/cm}^2$ , the increase of activation polarization from  $25^{\circ}\text{C}$  to  $-54^{\circ}\text{C}$  ( $-65^{\circ}\text{F}$ ) would be roughly 70 millivolts.

It could be argued that the transient currents measured in the tests represent the discharge of abnormally reactive material on the electrode surface. The true area of the test electrode is not precisely known but is probably about  $5 \text{ cm}^2/\text{cm}^2$  A.A. (based on one measurement of double layer capacity). The point at which voltage levels off in galvanostatic tests (Figure 6) corresponds to  $10^{-3}$  to  $4 \times 10^{-2}$  coulombs/cm<sup>2</sup> apparent area, and at the end of the one-half second current pulse the state of discharge is  $5 \times 10^{-3}$  to  $2 \times 10^{-1}$  coulombs/cm<sup>2</sup> A.A. Taking a rough value of  $0.2 \text{ millicoulombs/cm}^2$  as the capacity of a molecularly smooth surface of  $\text{Ag}_2\text{O}$ , the depth of discharge during the pulse is up to several hundred layers of  $\text{Ag}_2\text{O}$ . No radical increase in polarization occurs during this depth of discharge. The second conclusion is, therefore, that the high current densities are not due to an abnormal surface compound of 1 monolayer or less. Again, it could be argued that they arise from  $\text{Ag}_2\text{O}$  which is in contact with Ag in the preformed electrode, and that once the  $\text{Ag}_2\text{O}/\text{Ag}$  contact has been reacted a high ohmic resistance arises due to the necessity of electron transfer through  $\text{Ag}_2\text{O}$ . However, on cutting off the current pulse the same IR polarization is observed as on establishment of the current. There is no evidence of development of high IR polarization during the unsteady state discharge and it is probable that (a) reaction occurs via



dissolved  $\text{Ag}_2\text{O}$  or (b) that product silver always forms a bridge between  $\text{Ag}_2\text{O}$  and the silver matrix.

The pseudo steady-state results (Figure 4) indicate the existence of a limiting current (about  $175\text{-}200 \text{ ma/cm}^2$  A.A.). This limiting current was not affected by the rate of stirring and the third conclusion is that the electrode has a limiting current density which is not a consequence of mass transfer in the electrolyte. If the electrode mechanism involves dissolution of  $\text{Ag}_2\text{O}$ , this may produce a limiting rate. This postulate will be tested by measuring the rate of dissolution of  $\text{Ag}_2\text{O}$  under conditions of high mass transfer.

The pseudo steady-state results also show that polarization at a given current density increases as the surface is discharged. This is demonstrated in Figure 9, where the potential at a fixed current density is plotted as a function of the discharge of the electrode (100 coulombs represents about  $4 \times 10^5$  molecular layers of  $\text{Ag}_2\text{O}$  or about 0.1 mm.). The surface of the electrode was observed to be covered with a layer of black metallic silver when discharged to these extents. To compare the current density-voltage curves under identical states of surface discharge, the results of Figure 9 are replotted in Figure 10. The limiting current is more clearly delineated in this Figure but, more important, there is a steeper increase in polarization with increased current for curve b. The explanation of the lower performance of the electrode at increased degrees of discharge will be a primary aim of future work, since the explanation may enable electrodes to be designed to reduce this effect. In particular, the effect will be studied at lower temperatures to see if the decrease in performance becomes more severe at lower temperatures. The form of the

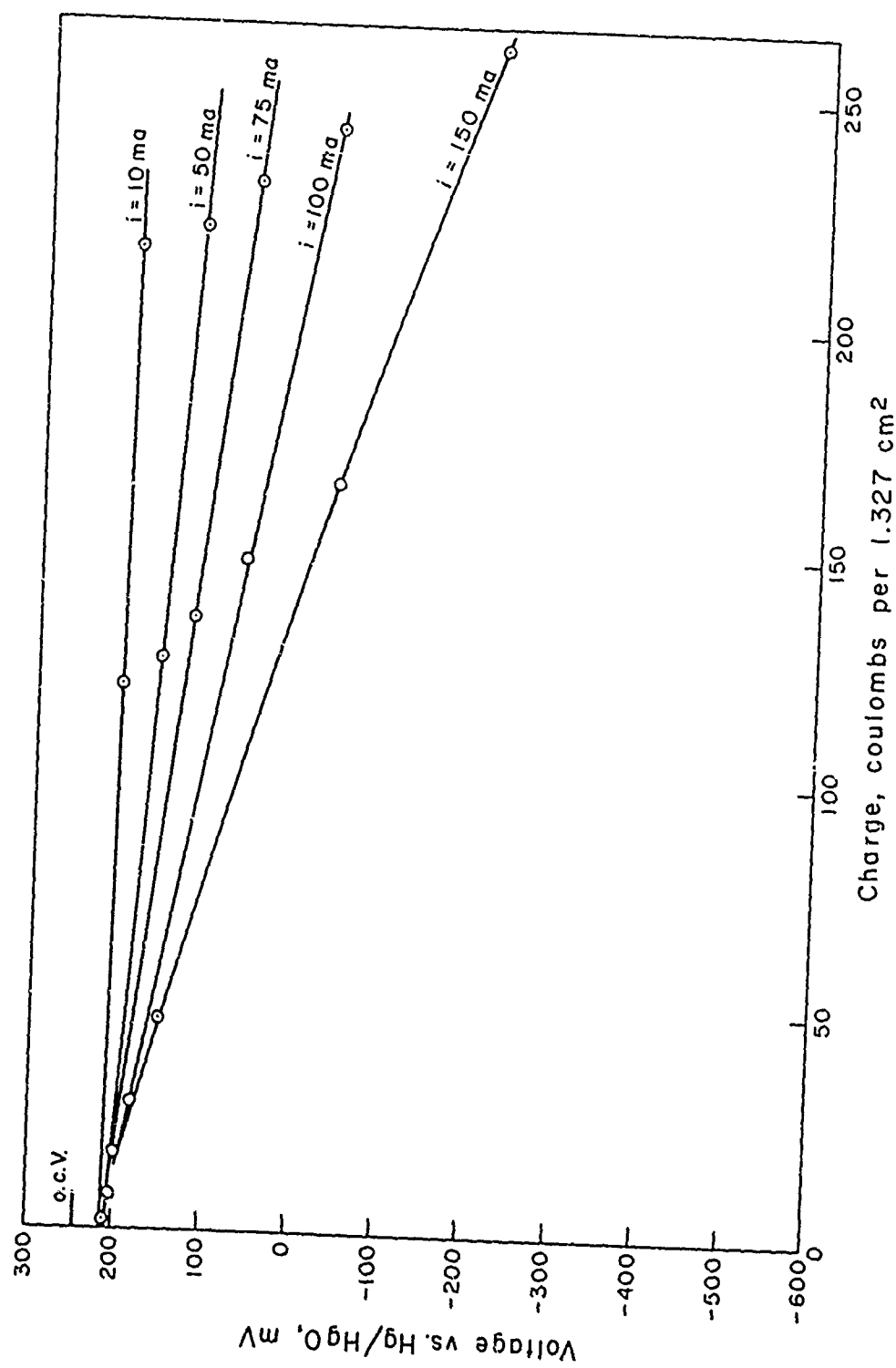


Fig. 9

Potential versus State of Discharge of the Electrode at Fixed Currents

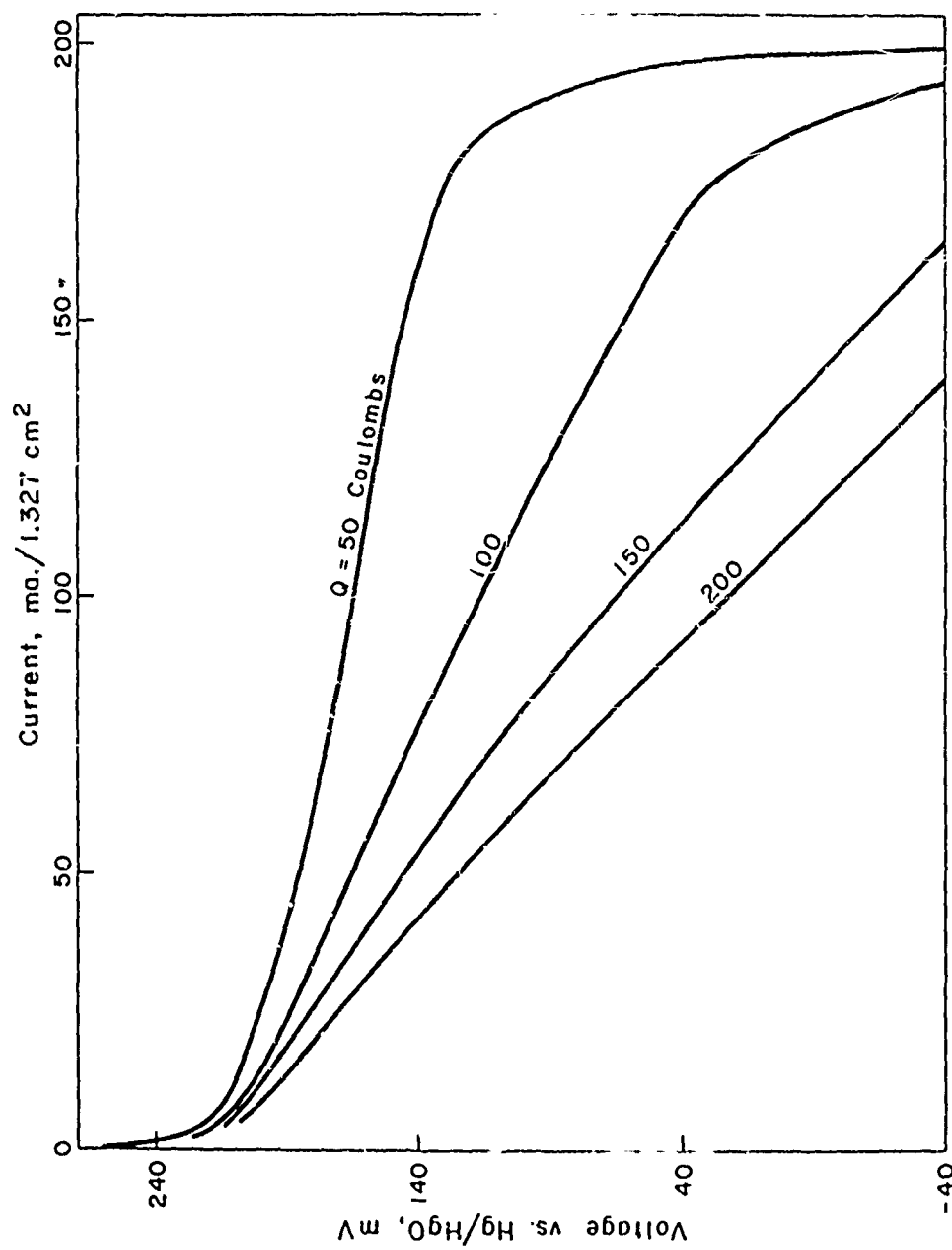


Fig. 10  
Current-Voltage Relation of  $\text{Ag}_2\text{O}/\text{Ag}$  Electrode  
as a Function of State of Discharge

results strongly suggest that the film of discharged material on the surface gives rise to IR polarization, since ions have to travel through electrolyte in the pores of the film. A rough calculation gives a film thickness of about 0.1 mm at 100 coulombs/cm<sup>2</sup> A.A. discharge. The current-voltage curve at this discharge suggests an ohmic resistance of about 1 ohm cm<sup>2</sup>. Taking 0.1 mm as the film thickness the effective resistivity is thus 100 ohm cm. This represents a labyrinth factor of about 50. It is planned to investigate the permeability of the film formed after long periods of discharge.

REVIEW OF FUNDAMENTAL INVESTIGATIONS OF  
SILVER OXIDE ELECTRODES

APPENDIX 1

Literature Survey of Recent Fundamental Investi-  
gations of Silver Oxide Electrodes.

1. "An X-ray Diffraction Study of the Anodic Oxidation of Ag in  $H_2SO_4$  Solution", Briggs, G. W. D., Dugdale, I. and Wynne-Jones, W. F. K., *Electrochimica Acta*, 4, 55 (1961).

- X-ray diffraction patterns of the anodic oxide layer on Ag have been obtained from oscillating Ag electrodes during polarization in  $H_2SO_4$  solution, and have been compared with those obtained from Ag in KOH and from an inert electrode in acid  $Ag_2SO_4$  solution. Powder photographs have also been obtained and the effect of decomposition of the oxides investigated. It is shown that the anodic oxide film formed on Ag in  $H_2SO_4$  solutions thickens considerably during continuous polarization and that both AgO and Ag "peroxy sulfate" are formed.

2. "Electrolytic Transition of  $Ag_2O$  to AgO in Alkaline Solutions", Dirkse, T. P. and Werkema, G. J., *J. Electrochemical Society*, 106, 88 (1959).

- An interrupted constant current technique was used to study the electrolytic oxidation of Ag in alkaline solutions. The short voltage peak just preceding the stage corresponding to the production of AgO in the voltage-time curves is interpreted as being due to the high electrical resistance to the  $Ag_2O$  layer.

3. "Controlled Potential Reactions of Cd and Ag in Alkaline Solution", Croft, G. T., *J. Electrochemical Society*, 106, 278 (1959).

- Data are reported on the electrochemical oxidation and reduction of both Cd and Ag in KOH electrolyte obtained using techniques in which the overpotential was the independent and the

current the dependent variable. The rate of oxidation of Cd is maximum at overpotentials of 18.0 and approximately 40.0 mV. The rate of reduction of Cd and the rate of oxidation of Ag are both monotonically increasing functions of the overpotential.

4. "The Stability and Solubility of AgO in Alkaline Solutions", Dirkse, T. P. and Wiers, B., J. Electrochemical Society, 106, 284 (1959).

- Silver oxide is stable in boiling water and decomposes but very little at room temperature in strongly alkaline solutions. The presence of  $\text{Ag}_2\text{O}$  does not affect this stability, but the presence of unoxidized Ag does increase the rate of decomposition. When AgO dissolves in strongly alkaline solutions the dissolved form is primarily AgO and  $\text{Ag}(\text{OH})_3^-$ . The standard free energy of formation of the latter is -85,380 cal/mol. (The AgO was analyzed both chemically and by X-ray diffraction.

5. "A Study of the Silver (I) Oxide-Silver (II) Oxide Electrode", Bank, J. F. and Garrett, A. R., J. Electrochemical Society, 106, 612 (1959).

- A reproducible emf of the cell  $\text{Ag}(\text{c}), \text{Ag}_2\text{O}(\text{c})/\text{NaOH}(\text{lm})/\text{AgO}(\text{c}), \text{Ag}_2\text{O}(\text{c}), \text{Pt}$  is found to be 0.262 V at 25°C. From this value and the known potential of the Ag,  $\text{Ag}_2\text{O}$  electrode, the standard oxidation potential of the  $\text{Ag}_2\text{O}, \text{AgO}$  electrode is -0.604 V. The temperature coefficient of the cell is  $+ 2.20 \times 10^{-1}$  V/deg. The free energy, enthalpy, and entropy changes for the cell reaction are -6049 cal, -4537 cal, and 5.07 cal/deg, respectively. From these values and the existing thermodynamic data on Ag and  $\text{Ag}_2\text{O}$ , values of 3463 cal,

-2769 cal, and 13.81 cal/deg are calculated, respectively, for the free energy and enthalpy of formation and for the entropy of AgO at 25°C.

6. "Oxides on the Silver Electrode", Wales, C. P. and Burbank, J., J. Electrochemical Society, 106, 885 (1959).

- Ag electrodes were studied by means of potentials and X-ray diffraction patterns. The Ag was charged anodically in 35% KOH by means of either constant current or constant potential, and discharged at a low or high rate. Attempts were made to form an oxide higher than AgO by means of anodization. The products of anodization of Ag in 2N H<sub>2</sub>SO<sub>4</sub> were determined. The basis for the theory that the oxides of Ag are formed by the introduction of O<sub>2</sub> into the octants of the face-centered cubic Ag lattice was examined.

7. "The Oxidation of the Ag Electrode in Alkaline Solutions", Dirkse, T. P., J. Electrochemical Society, 106, 920 (1959).

- The formation of Ag<sub>2</sub>O and AgO was studied by means of constant current and constant potential processes. The efficiency of these oxide formations was determined by measuring the gain in weight of Ag electrodes under various conditions of charge, and the extent of the polarization of these processes was measured by using an interrupted current technique.

8. "The Silver-Silver Oxide Electrode", Cahan, B. D., Ockerman, J. B., Amlie, R. F., and Rüetschi, P., J. Electrochemical Society, 107, 725 (1960).

- An a-c square wave technique was used to study resistance



and double-layer capacity during film formation on Ag electrodes in KOH solutions. The peak in the voltage-time curve at constant current anodization is shown to coincide with complete surface coverage by  $\text{Ag}_2\text{O}$  and is not an ohmic resistance, but rather an overvoltage effect. Evidence for the existence of an unstable higher oxide than AgO (or additional oxygen) during  $\text{O}_2$  evolution is presented. Microvolumetric gas measurements with large area electrodes on open circuit decay also support this conclusion. The duration of the upper voltage plateau of the voltage-time curve during discharge of AgO electrodes is determined by contact phenomena among individual AgO particles, in particular by separation and passivation of the remaining AgO by insulating surface layers of  $\text{Ag}_2\text{O}$ .

9. "The Cathodic Behavior of AgO in Alkaline Solutions", Dirkse, T. P., J. Electrochemical Society, 107, 859 (1960).

- A study has been made of the discharge of AgO to determine why only a part of the discharge capacity of AgO is delivered at the potential of the AgO- $\text{Ag}_2\text{O}$  couple and to determine the role of  $\text{O}_2$  in this process. The difference in discharge capacity of electrodes produced by constant-current and by constant-potential anodization also has been studied. A mechanism involving the transport of  $\text{O}^=$  ions through the electrode material and the reaction of these ions with the electrolyte is discussed.

10. "The Silver-Silver Oxide Electrode: I. Anodic Oxidation in Alkaline Solutions", Wales, C. P., J. Electrochemical Society,

108, 395 (1961).

- Ag electrodes were oxidized anodically at 25°C in 35 or 50% KOH at constant charge currents that ranged from  $\frac{1}{2}$  to 40 hr. rates. The electrodes were given both partial and complete charges. Except at low charging rate the capacity was higher in 35% KOH than at 50% KOH. Oxidation was highly efficient at the first two potential plateaus. During a charge at the  $\text{Ag}_2\text{O}/\text{AgO}$  plateau initially  $\text{Ag}_2\text{O}$  oxidizes to  $\text{AgO}$  and then the prevailing reaction is  $\text{Ag}$  oxidizing to  $\text{AgO}$ . Simultaneously some  $\text{AgO}$  reacts with  $\text{Ag}$  to give  $\text{Ag}_2\text{O}$ . Under certain discharge conditions  $\text{AgO}$  may reduce directly to  $\text{Ag}$ , with  $\text{Ag}_2\text{O}$  forming as a secondary product.

11. "Solubility and Stability of Silver Oxides in Alkaline Electrolytes", Amlie, R. F. and Ruetschi, P., J. Electrochemical Society, 108, 813 (1961).

- The solubility of  $\text{Ag}_2\text{O}$  and  $\text{AgO}$  in alkaline electrolytes has been studied with a polarographic technique, using a rotating Pt electrode. Only a monovalent (and no divalent) silver species could be detected in solutions which had been in intimate contact with  $\text{AgO}$  powder over prolonged periods of time.

Quantitative measurements of the solubility of  $\text{Ag}_2\text{O}$  in KOH ranging from 1-14 moles/liter, were carried out utilizing a potentiometric titration method. The solubility has a maximum at about 6N KOH where it reaches a value of  $4.8 \times 10^{-4}$  N.

The rate of the decomposition reaction  $2\text{AgO} \rightarrow \text{Ag}_2\text{O} + \frac{1}{2}\text{O}_2$  in alkaline electrolytes was investigated with a very sensitive microvolumetric method. The reaction rate increases with increasing  $\text{OH}^-$

ion concentration and is sensitive to day-light. The decomposition seems to proceed at the solid-liquid interface. Any divalent Ag dissolving in minute amounts into the electrolyte is decomposed rapidly due to its instability. The decomposition proceeds at a rate of about 16% in 1 year at 30°C and 49% in 1 year at 45°C. This reaction can contribute significantly to the self-discharge of AgO-Zn batteries.

12. "The Structure of Silver Oxide Determined by Means of Neutron Diffraction", Scatturin, V., Bellon, P. L. and Solkind, A. J., J. Electrochemical Society, 108, 819 (1961).

- The crystal structure of AgO has been determined by means of neutron diffraction. The nuclear scattering of Ag and O atoms has made it possible to determine the positions of the O atoms and to modify the space group which was reported for this compound from X-ray data. No magnetic diffractions were observed even at liquid He temperature; the absence of magnetic scattering confirms the diamagnetism of the compound. The lattice was found to be monoclinic, space group  $P2_1/C$ , with four formula weights of AgO in the unit cell. The Ag atoms are not equivalent and in the structure there are two Ag-O distances of 2.18 Å and 2.03 Å; the first one corresponds to colinear Ag(1)-O bonds, the second distance corresponds to square planar Ag(111)-O bonds.

13. "Investigation of the Ag-Zn Storage Battery with Radioactive Ag<sup>110</sup> Isotope", Palagyi, T. Z., J. Electrochemical Society, 108, 904 (1961).

- The batteries were assembled in three ways, 1) loosely, 2) normally, 3) tightly, with one Ag electrode in the middle containing the  $\text{Ag}^{110}$ . The cells were then cycled and all the electrodes were examined for  $\text{Ag}^{110}$ . In 3) the degree of contamination of the electrodes by  $\text{Ag}^{110}$  was higher than in 1) or 2). In 1) and 2) there was some contamination of the other electrodes. Battery failure resulted from a number of causes, namely, disintegration of the separators, formation of acicular Zn crystals and short circuits from Zn sponge formation.

14. "Factors Affecting the Transport of Ag in Ag-Alkaline Batteries", Dirkse, T. P. and VanderLugt, L. A., J. Electrochemical Society, 111, 629 (1964).

- A study has been made of the factors which control the amount of Ag which is introduced into the electrolyte during the operation of a Ag-alkaline battery. Part of this work was done with the use of radioactive Ag as a tracer. Silver is introduced into the electrolyte during all phases of the operation of a Ag-alkaline battery. However, it can be increased by charging at lower current densities or by operation at the  $\text{Ag}/\text{Ag}_2\text{O}$  voltage level. A possible mechanism for the electrolytic formation of the oxides is also given.

15. "Oxides on the Silver Electrode-II. X-Ray Diffraction Studies of the Working Silver Electrode", Wales, C. P. and Burbank, J., J. Electrochemical Society, 112, 13 (1965).

- Silver electrodes were examined in 20-50% KOH using a cell

permitting simultaneous X-ray diffraction and electrochemical studies. Highly oriented smooth rolled sheet Ag developed randomly oriented Ag on its surface during early cycles. Charge-discharge capacity increased to a maximum as surface area increased. AgO crystal size and amount formed varied inversely with charging c.d. High charge rates gave tight coatings of small AgO crystals that limited further oxidation. Reactions took place initially at the outer surface of the electrode. Oxidation to  $\text{Ag}_2\text{O}$  and AgO and reduction to  $\text{Ag}_2\text{O}$  and Ag occurred by formation of distinct crystals rather than expansion or contraction of preexisting crystal lattices. Discharge capacity at the AgO/ $\text{Ag}_2\text{O}$  potential plateau depended more on surface area than on quantity of AgO. A slow discharge produced smoother Ag surfaces, lowering capacity of the next cycle. There was never evidence of a suboxide, oxidation state higher than AgO, solid solution, or alloy of oxygen and silver.

16. "On the Determination of the Roughness of Metallic Surfaces", Wagner, C., J. Electrochem. Soc., 97, 71 (1950).

- It is shown that polarization capacity of an electrode can be measured rapidly with the aid of a ballistic galvanometer. The polarization capacity per unit apparent area can be considered approximately proportional to the roughness of the surface of the electrode. Results obtained on Ag electrodes illustrate the influence of pretreatment and aging.

17. "A Reproducible and Stable Silver-Silver (I) Oxide Electrode", Hamer, W. J. and Craig, D. N., J. Electrochem. Soc., 104, 206 (1957).

- A method is described for the preparation of silver-silver oxide electrodes which are stable and reproducible. When used in cells of the type  $\text{Hg}(\ell)$ ,  $\text{HgO}(\text{s})/\text{NaOH, aq.}/\text{Ag}_2\text{O}(\text{s})$ ,  $\text{Ag}(\text{s})$  the silver-silver oxide electrodes give stable potentials over periods of 38 days. No evidence was found that  $\text{Ag}$ ,  $\text{Ag}_2\text{O}$  electrodes evolve  $\text{O}_2$ , that  $\text{Ag}_2\text{O}$  exists in different forms in aqueous solutions at normal temperatures, that  $\text{Ag}_2\text{O}$  reverts to a lower oxide, or that imperfections exist in the  $\text{Ag}_2\text{O}$  crystal. The free energy and entropy changes for the reaction in the above cell are -11254 cal. and -9.12 e.u., respectively, at  $25^\circ\text{C}$ . These values are reasonably consistent with the best available thermodynamic data. The standard electrode potential of the  $\text{Ag}$ ,  $\text{Ag}_2\text{O}$  electrode is found to be 0.342 V at  $25^\circ\text{C}$ .

18. "Reaction of Silver Oxides with KOH", Dirkse, T. P., et al., J. Inorg. Nucl. Chem., 25, 859 (1963).

- The dissolution of silver oxides in aqueous KOH solutions was followed by determining solubility and by observing the changes in potential of a silver electrode in such solutions. The effect of solubility with time was studied and the identity of the black decomposition product was determined. The extent to which silver oxides dissolve in aqueous KOH is determined by several reactions.

19. "Electrooptical Systems, Contract NAS7-181, Final Report, July 1963.

- The resistance of  $\text{Ag}_2\text{O}$  powder was found to be  $10^3$  ohm and did not agree with literature values ( $10^8$  ohm). Doping of  $\text{Ag}_2\text{O}$  by coprecipitating divalent oxides (e.g.  $\text{CoO}$ ) with  $\text{Ag}_2\text{O}$  produced little

effect on cell performance. The first charge of Ag to  $\text{Ag}_2\text{O}$  was only 20% complete before the electrode went to the  $\text{AgO}/\text{Ag}_2\text{O}$  potential, but on repeated charge and discharge this value was increased to 55-65%.

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